

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-066600

(43)Date of publication of application : 19.03.1993

(51)Int.Cl.

G03G 9/08  
G03G 9/087

(21)Application number : 03-224227

(71)Applicant : DAINIPPON INK &amp; CHEM INC

(22)Date of filing : 04.09.1991

(72)Inventor : TASHIRO NAMİYUKI  
TAKAYANAGI HITOSHI  
SHINTO HIROKO

## (54) CAPSULE TYPE TONER AND PRODUCTION THEREOF

## (57)Abstract:

PURPOSE: To obtain the capsule type toner particles which do not contain a dispersion stabilizer and are dispersed with coloring agents uniformly in the particles by the simple process and to obtain desired characteristics (electrostatic chargeability, flow property, fixability, etc.) by easily controlling the grain sizes with the quantity of the bases to neutralize the acid groups, forming a grain size distribution to a normal distribution and using various kinds of anion type self-water dispersible resins.

CONSTITUTION: This capsule type toner is formed by including the coloring agents into the anion type self-water dispersible resins. This process for production of the capsule type toner consists of a 1st stage for mixing and dispersing both components consisting of, 100 parts anion type self-water dispersible resins and 2 to 150 parts coloring agents, a 2nd stage for forming the capsulated particles in an aq. medium by phase transition emulsification thereof and a 3rd stage for separating the formed capsule particles from the aq. medium and drying the particles.

## LEGAL STATUS

[Date of request for examination] 06.07.1998

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration] 2

[Date of final disposal for application]

[Patent number] 3063269

[Date of registration] 12.05.2000

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

[Claim(s)]

[Claim 1] The capsule mold toner with which the endocyst of the coloring agent was carried out to anion mold self-water-dispersion resin.

[Claim 2] The manufacture approach of the capsule mold toner characterized by to consist of the first process which makes the mixed constituent containing anion mold self-water-dispersion resin and a coloring agent distribute, the second process which make the particle encapsulated in the water medium by carrying out phase-inversion emulsification of said distributed constituent generate, and the third process which separate the capsule particle which generated in said water medium out of a water medium, and make dry.

[Claim 3] The first process which makes the mixed constituent containing anion mold self-water-dispersion resin and a coloring agent distribute, and by carrying out phase inversion emulsification of said distributed constituent. Consist of the second process which makes the particle encapsulated in the water medium generate, and the third process which separates the capsule particle generated in said water medium out of a water medium, and is made to dry, and, moreover, it sets after this phase inversion emulsification. The manufacture approach of the capsule mold toner characterized by making the neutralized acid radical reverse-neutralize.

[Claim 4] The above mentioned anion mold self-water-dispersion resin Acid radical content polymerization nature monomers It is the copolymer obtained using one sort of compounds. it is chosen out of the group which consists of acid radical content polymerization nature oligomer, polymerization nature monomers which do not contain an acid radical, and polymerization nature oligomer which do not contain an acid radical -- few -- \*\* -- And the capsule mold toner according to claim 1 which is what has the 20-500mg [ per 100g ] acid radical of resin solid content.

[Claim 5] The above mentioned anion mold self-water-dispersion resin Acid radical content polymerization nature monomers It is the copolymer obtained using one sort of compounds. it is chosen out of the group which consists of acid radical content polymerization nature oligomer, polymerization nature monomers which do not contain an acid radical, and polymerization nature oligomer which do not contain an acid radical -- few -- \*\* -- And the manufacture approach of the capsule mold toner according to claim 2 or 3 which is what has the 20-500mg [ per 100g ] acid radical of resin solid content.

[Claim 6] said anion mold self-water-dispersion resin carried out is chosen from the group which consists of a carboxyl group, a phosphate group, a sulfonic group, and a sulfuric-acid radical -- few -- \*\* -- the capsule mold toner according to claim 1 or 4 which is what has one sort of acid radicals.

[Claim 7] said anion mold self-water-dispersion resin carried out is chosen from the group which consists of a carboxyl group, a phosphate group, a sulfonic group, and a sulfuric-acid radical -- few -- \*\* -- the manufacture approach of the capsule mold toner according to claim 2, 3, or 5 which is what has one sort of acid radicals.

[Claim 8] The manufacture approach of the capsule mold toner according to claim 2 or 3 which consists of making the electrification control agent of 0.1 - 5 weight section add further in the first above mentioned process.

[Claim 9] The manufacture approach of the capsule mold toner according to claim 2 or 3 which consists of making the release agent of 0.1 - 5 weight section add further in the first above mentioned process.

[Claim 10] The manufacture approach of the capsule mold toner according to claim 2 or 3 which consists of making magnetic powder add further in the first above mentioned process.

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is made new and relates to a useful capsule mold toner and its manufacture approach. Furthermore, anion mold self-water-dispersion resin and a coloring agent are used for a detail as an indispensable component, respectively. It is related with the capsule mold toner which is obtained and with which the endocyst of the coloring agent was carried out to anion mold self-water-dispersion resin. Fundamentally The first process which makes the mixed constituent containing both such components distribute, and by carrying out phase inversion emulsification of said distributed constituent It is related with the manufacture approach of the toner which divides and is used as an object for the development of an electrostatic latent image which consists of the second process which makes the particle encapsulated in the water medium generate, and the third process which separates the capsule particle generated in said water medium out of a water medium, and is made to dry.

[0002]

[Description of the Prior Art] As a fine-particles toner for using an electrostatic latent image as a visible image, the resin for toners is made to distribute additives, such as a coloring agent, a release agent, and an electrification control agent, by melting mixing, this is mechanically ground after cooling, and what is obtained by making it classify is common the appropriate back.

[0003] However, the toner obtained by such approach, The lowness of the instability of the electrical property for the ability not to cover with resin completely and the yield in the case of attaining diameter-ization of a granule and the various problems [ say / the lowness of the limitation of a coloring agent addition etc. ] which are not desirable are further connoted above all like [ in case coloring agents are the variation in the electrical property produced from mixed unevenness / a coloring agent or a release agent /, fluid badness for particle shape to be an indeterminate form, and conductivity like carbon ].

[0004] moreover, preparation of a toner -- the time -- carrying out -- even if -- the above approaches -- having followed -- a case -- \*\*\*\* -- melting kneading and grinding -- requiring -- electrical energy -- consumption is great. as the future toner for high resolving -- 5 microns (micrometer) -- although diameter[ of a granule ]-izing (the present condition is 10-15 micrometers.) of level and high concentration-ization of a coloring agent are especially needed, it is the actual condition which is referred to as being unable to oppose by the so-called grinding method after all.

[0005] It has succeeded in an examination according to various kinds of polymerization methods also as approaches other than the above-mentioned grinding method. For example, the approach by the suspension-polymerization method is proposed by JP,57-53756,A, JP,59-161,A, and JP,59-123851,A.

[0006] Although this suspension-polymerization method distributes a coloring agent, an additive, etc. in a monomer (monomer) and it is said for the polymerization of this under high shear in an aqueous medium to the bottom of existence of a suspension stabilizer that it carries out the appropriate back, these coloring agents, additives, etc. are difficult for there to be nothing and for stability to carry out mixed distribution to the thing of hypoviscosity like a monomer moreover in a monomer and the thing which not necessarily has compatibility.

[0007] Therefore, it shifts to the aqueous phase during a polymerization, and it sometimes even lapses into the situation where neither a coloring agent nor an additive exists in a polymer particle, and there is sometimes a fault of not accompanying at mind, surely.

[0008] Moreover, contrary to it, a coloring agent may condense during a polymerization, the block object of a coloring agent may arise, and it may become the panel where heterogeneity is puffed up. Especially the coloring agent with a small particle size of the primary particle like carbon serves as a place which may be quite firm

secondary floc, and causes distributed aggravation into a monomer, as a result expands the variation in the electrification property of a toner particle, and the variation of image concentration.

[0009] Furthermore, a suspension stabilizer may exist in a particle front face, and removal may become difficult, consequently it may have a bad influence on a fluidity or an electrification property. Of course, although it is possible to also make a suspension stabilizer wash depending on the case, existence of the trouble of becoming high in cost cannot be denied.

[0010] Independently, the approach by the emulsion-polymerization method is proposed by a U.S. Pat. No. 3,391,082 specification and JP,61-167955,A, JP,61-167956,A, and JP,61-167957,A.

[0011] It is difficult for an emulsion-polymerization method to also have a problem in mixed distribution with a coloring agent, an additive, and a monomer, and to make homogeneity connote it in a particle. [ as well as a suspension-polymerization method ] Furthermore, in order to use a distributed stabilizer so much, an electrical property and the effect on a fluidity are large, and cost also starts washing.

[0012] Moreover, since the path of the particle to generate is small, concomitant use with a coagulant is required and a problem remains also in respect of control of particle diameter. The approach by the nonaqueous distribution polymerization method is proposed by JP,61-249816,A or JP,63-100466,A.

[0013] Although this nonaqueous polymerization method is an approach of making this organic solvent remove after adding and carrying out the polymerization of a coloring agent, a distributed stabilizer, and the monomer to the organic solvent which has larger SP value than the soluble parameter (SP value) of the resin to generate, essentially, it is difficult the method like a suspension-polymerization method to make homogeneity contain a coloring agent and an additive in a particle.

[0014] Moreover, constraint is received in the presentation of resin, the class of solvent, and the class of a coloring agent, additive, etc., and control of a polymerization becomes complicated. Furthermore, in washing in order to use a distributed stabilizer, it also has too the trouble that cost becomes high.

[0015] Although the amelioration means by various polymerization methods is also \*\*\*\*(ed) as the so-called amelioration of the grinding method, including a coloring agent, an additive, etc. in homogeneity in a particle has reached to an extreme of difficulty from the place which carries out mixed distribution of a monomer, a coloring agent, the additive, etc., and all performs a polymerization.

[0016] Moreover, addition of a distributed stabilizer is indispensable and the effect which it has on the electrical property and fluidity by the addition is unescapable surely. And the present condition is that a manufacture process becomes complicated, moreover produce the fault resulting from a manufacture process also by the polymerization method, and the toner which should be satisfied is not fully obtained conventionally as great cost will start, if it is going to wash this distributed stabilizer.

[0017]

[Problem(s) to be Solved by the Invention] Thus, as long as the conventional technique was followed, the actual condition was that fundamental properties, such as the electrification property that it was released from the complicatedness of a manufacture process and the coloring agent was distributed by homogeneity in the particle, a fluidity, and fixable, can never obtain the satisfied toner entirely.

[0018] However, this invention persons have already proposed a different completely new capsulation means from the grinding method and a polymerization method which were mentioned above on the Japanese-Patent-Application-No. No. 260025 [ two to ] specifications.

[0019] In case this manufactures the minute capsule which makes resin come to include a hydrophobic liquid and/or the hydrophobic individual matter, under an operation of a water medium Mean particle diameter makes a minute capsule form in a level 0.1 micrometers or less using the so-called self-dispersibility resin which has the dispersion power which carries out self-distribution. By it It is the approach of performing substantially atomization into a water medium, and formation-ization of a capsule wall to coincidence, and in not using a distributed stabilizer and moreover manufacturing this capsule mold toner as a means of capsulation, it has the advantage in which the need does not carry out special equipment.

[0020] In such invention proposed previously, the application of such a new capsule mold toner was not described about a presentation or the manufacture approach of concrete resin at all.

[0021] Therefore, even if the place made into the purpose of this invention does not solve the trouble in the \*\*\*\* grinding method and polymerization method which were mentioned above by using a means which was proposed previously and it does not use a distributed stabilizer especially, it is to say that the approach of preparing the capsule mold toner which connoted the coloring agent to homogeneity in the particle according to a very simple process is offered.

[0022] Therefore, the technical problem which this invention tends to solve is also offering the approach of

offering and combining the capsule mold toner which connoted the coloring agent to homogeneity in the particle according to a very simple process, without using a distributed stabilizer, and preparing the capsule mold toner.

[0023]

[Means for Solving the Problem] Then, by this invention persons' doubling collimation with \*\*\*\* Object of the Invention mentioned above, and using special resin called anion mold self-water-dispersion resin, as a result of repeating examination wholeheartedly Even if it did not use a distributed stabilizer, it reaches for finding out that the capsule mold toner which connoted the coloring agent to homogeneity in the particle can be prepared according to a very simple process, and came to complete this invention here.

[0024] This invention is what first offers the capsule mold toner with which the endocyst of the coloring agent was carried out to anion mold self-water-dispersion resin. Namely, fundamentally The first process which makes the mixed constituent containing both such components distribute, and by carrying out phase inversion emulsification of said distributed constituent The manufacture approach of the capsule mold toner which consists of the second process which makes the particle encapsulated in the water medium generate, and the third process which separates the capsule particle generated in said water medium out of a water medium, and is made to dry is also offered.

[0025] Below, this invention is explained at a detail. First, the anion mold self-moisture acidic resin used in this invention is explained.

[0026] The acid radical used as a hydrophilic group is introduced into resin through the chemical bond, it is that this acid radical is neutralized by an organic base or the inorganic base, and serves as an anion in a water medium, and presents a hydrophilic property.

[0027] If it limits for illustrating only a typical thing especially as this acid radical, they will be a carboxyl group, a phosphate group, a sulfonic group, or a sulfuric-acid radical. After adding a base to the organic continuous phase (O phase) which dissolved the resin which has this acid radical in the organic solvent and neutralizing, by throwing in a water medium (W phase), conversion (the so-called phase inversion emulsification) of resin to O/W from W/O is performed, it discontinuous-phase-izes, and distributed stabilization of the resin is carried out into a water medium at the shape of a particle.

[0028] The resin which has such a property is the so-called anion mold self-water-dispersion resin.

[0029] In this invention, the anion mold self-water-dispersion resin concerned will form a capsule particle. What is made to copolymerize the polymerization nature monomers which have an acid radical, and polymerization nature monomers other than these acid radical content polymerization nature monomers under existence of a polymerization initiator as the resin concerned used by this invention, and is obtained is mentioned.

[0030] If it limits for illustrating only a typical thing especially as such acid radical content polymerization nature monomers, they will be an acrylic acid, a methacrylic acid, a crotonic acid, an itaconic acid, a maleic acid, a fumaric acid, itaconic-acid monobutyl, maleic-acid monobutyl, acid phosphoxyethyl methacrylate, acid phosphoxypropyl methacrylate, 3-chloro-2-acrylamido-2-methyl propane sulfonic acid, or 2-sulfoethyl methacrylate.

[0031] if it limits for illustrating only a typical thing especially as polymerization nature monomers other than acid radical content polymerization nature monomers -- various kinds of styrene system monomer (aromatic series vinyl monomer); like styrene, vinyltoluene, 2-methyl styrene, t-butyl styrene, or KURORU styrene

[0032] Various kinds of acrylic ester like a methyl acrylate, an ethyl acrylate, acrylic-acid isopropyl, acrylic-acid n-butyl, isobutyl acrylate, acrylic-acid n-amyl, acrylic-acid isoamyl, acrylic-acid n-hexyl, 2-ethylhexyl acrylate, acrylic-acid n-octyl, acrylic-acid DESHIRU, or acrylic-acid dodecyl;

[0033] Various kinds of methacrylic ester like a methyl methacrylate, methacrylic-acid propyl, n-butyl methacrylate, methacrylic-acid isobutyl, methacrylic-acid n-amyl, methacrylic-acid n-hexyl, 2-ethylhexyl methacrylate, n-octyl methacrylate, methacrylic-acid DESHIRU, or methacrylic-acid dodecyl; various kinds of hydroxyl (hydroxyl group) content monomers like acrylic-acid hydroxyethyl or methacrylic-acid hydroxypropyl;

[0034] Or they are various kinds of N-permutation (meta) acrylic monomers like N-methylol (meta) acrylamide or N-butoxy methyl (meta) acrylamide.

[0035] The copolymer obtained in this way may be a copolymer with polymerization nature monomers and polymerization nature partial saturation radical content oligomer depending on the case. Furthermore, what has an acid radical may be used into this polymerization nature partial saturation radical content oligomer.

[0036] As the above-mentioned polymerization nature partial saturation radical content oligomer, vinyl denaturation polyester, vinyl denaturation urethane, or a vinyl denaturation epoxy compound is especially typical.

[0037] Specifically, a polymerization nature unsaturated bond (vinyl group) is introduced by the polycondensation of various kinds of compounds or addition like a maleic anhydride, a fumaric acid, tetrahydro phthalic anhydride

and a methylene tetrahydro maleic anhydride, alpha-terpinene maleic-anhydride addition product, the monoallyl ether of triol, pen TAERI slit diaryl ether, or allyl glycidyl ether.

[0038] Furthermore, in order to make an acid radical introduce into polyester, what what has a carboxyl group at the end is obtained by it that what is necessary is just because the dibasic acid like a phthalic acid is used superfluously, or has an acid radical in a principal chain by use of trimellitic anhydride is obtained.

[0039] Moreover, as the above-mentioned vinyl denaturation urethane, it is obtained by the addition polymerization of the various kinds of polyols and diisocyanate including glycerol monoallyl ether or 1. and 2-association like butadiene polyol etc., for example.

[0040] Or vinyl association is introduced into an end by the addition reaction of the urethane and the hydroxyl-group content polymerization nature monomers which have an isocyanate radical etc. Moreover, an acid component can be made to introduce into polyurethane also by adding dimethylol propionic acid etc. as a polyol component.

[0041] as the mono-methacrylate of a polyethylene glycol -- the average molecular weight of for example, a polyoxyethylene chain -- 1,000-4,000 -- a thing within the limits is mentioned.

[0042] Moreover, for example, an acid component can be made to introduce also by this as a vinyl denaturation epoxy compound that what is necessary is just to make an end epoxy group and the carboxyl group of an acrylic acid or a methacrylic acid react.

[0043] Furthermore, the oligomer of the polymerization nature monomers which have the polymerization nature vinyl group which made the glycidyl group content polymerization nature monomer add to a carboxyl group content vinyl copolymer is obtained.

[0044] The polymerization nature monomers used here are chosen from what was shown above.

[0045] In addition, it is marketed as a macro monomer, for example, the oligomer of end vinyl denaturation made from Toagosei Chemical industry can also be used. Needless to say, if it is the oligomer which has a polymerization nature vinyl group, it will not be limited to the class or approach which were mentioned above.

[0046] The polymerization in this case is usually performed using a polymerization initiator. As this polymerization initiator, of course, although the usual thing can be used, if it limits for illustrating only what [ those ] are especially typical also by striking, they will be various kinds of azo compounds [ like / various kinds of peroxides; like a benzoyl peroxide G t-butyl peroxide, cumene hydroperoxide, t-butyl peroxide, or 2-ethylhexanoate, azobisisobutyronitril, or azobisiso valeronitrile ] etc.

[0047] Moreover, if it limits for illustrating only an especially typical thing as a reaction solvent Various kinds of aromatic hydrocarbon [ like / toluene, a xylene, or benzene ]; A methanol, Various kinds of alcohols [ like / ethanol, propanol, or a butanol ]; like cellosolve or carbitol Various kinds of ether alcohol; like an acetone, a methyl ethyl ketone, or methyl isobutyl ketone Various kinds of ketones; they are the so-called inactive solvents, such as various kinds of ether ester like various kinds of ester; like ethyl acetate or butyl acetate, or butyl-cellosolve acetate.

[0048] Preferably, in the third process of \*\*\*\* mentioned later, use of the so-called low boiler of the acetone by which desolventization may be carried out easily, a methyl ethyl ketone, or ethyl acetate is appropriate.

[0049] Although polymerization conditions are the temperature requirements which become 50-150 degrees C and are usually performed under nitrogen-gas-atmosphere mind, of course, they are not limited only to this. And as an amount of the acid radical in the copolymer obtained, within the limits which 20-500mg equivalent / 100g of resin solid content become is suitable.

[0050] Since the hydrophilic property of the resin obtained is surely inadequate even if it neutralizes more than 100 mol % by the base when 20mg equivalent / resin solid content has less amount of the acid radical used than 100g, phase inversion emulsification cannot be carried out, therefore a capsule particle cannot be formed.

[0051] It is not desirable in [ since the hydrophilic property of resin is high when there is more 500mg equivalent / resin solid content than 100g ] the place where particle formation in a water medium becomes unstable to this case on the other hand, either.

[0052] In this way, if the amount of an acid radical is within the limits which 20-500mg equivalent / 100g of resin solid content become, by neutralizing some or all of an acid radical by the base, phase inversion emulsification can be carried out and a stable capsule particle can be formed.

[0053] moreover, the thing which has the molecular weight of the level which becomes enough as a capsule wall since the copolymer containing an acid radical serves as a capsule particle -- usually -- 3,000-100,000 -- within the limits -- desirable -- 5,000-50,000 -- it has number average molecular weight within the limits.

[0054] Preferably [ when molecular weight is smaller than 3,000 / since the property as a capsule wall cannot fully be demonstrated ] on the other hand, in being larger than 100,000 If viscosity becomes high too much, it

becomes inadequate distributing [ of the coloring agent in the first process mentioned later ] and it pulls The place which the degree (how to go up viscosity) of thickening at the time of the phase inversion emulsification in the second process becomes large, consequently will affect control of particle size, distribution (particle size distribution) of particle size, etc. to neither of the cases is desirable.

[0055] Moreover, in order to prevent the welding at the time of desiccation, or the blocking under hot environments, use of resin with a high glass transition temperature is desirable. Within the limits which 30-80 degrees C of use of resin with a low glass transition temperature of a capsule wall become from a desirable place as a glass transition temperature of the anion self-water-dispersion resin concerned in respect of heat fixable on the other hand is suitable.

[0056] Various kinds of epoxy compounds which are urethane resin, for example, urethane resin dispersion as shown in JP,1-287183,B, as the anion self-water-dispersion resin concerned used by this invention other than the above resin, or are described by an epoxy resin, for example, JP,53-1228,A, No. 3481 [ 55 to ], or 55 No. - 9433 official report are mentioned.

[0057] of course -- if it is anion mold self-water-dispersion resin -- mentioning above -- supra -- it is not limited to a thing the bottom. as the preparation approach of the capsule mold toner of this invention, it mentions above in the first process first -- having -- supra \*\*\*\*\* -- anion mold self-water-dispersion resin [ like ] is used.

[0058] Although this first process cheats out of a coloring agent to the anion mold self-water-dispersion resin used as an encapsulant, as that decentralization means, the means of well-known common use of a roll mill, a sand mill, etc. is suitable for it, and it should just carry out detailed decentralization with the means of such everything.

[0059] In here, as a coloring agent used by this invention, although a color, a pigment, etc. which have been used as a toner ingredient are used, until now If it limits for illustrating only a typical thing especially also among them, zinc yellow, Synthetic Ochre, a HANZA yellow, a JISUAZO yellow, a quinoline yellow, A permanent yellow, Permanent Red, a red oxide, Lithol Red, Although it is various kinds of pigments or oil solubility colors like pyrazolone red, Lake Red C, Lake Red D, brilliant carmine 6B, brilliant carmine 3B, Berlin blue, a copper phthalocyanine blue, a non-metal phthalocyanine, titanium oxide, or carbon black etc. however -- the toner of a black system -- magnetic powder -- with, it can consider as instead of [ of the coloring agent concerned ].

[0060] If it limits for illustrating only a typical thing especially as this magnetic powder, they will be various kinds of metaled alloys or compounds (compound of simple substance itself) like zinc [ like / various kinds of ferrites, magnetite, or hematite ], cobalt, nickel, or manganese etc.

[0061] such magnetic powder -- the shape of the shape of the shape (cube) of a globular shape and cubic, and a regular octahedron, and a needle etc. -- you may be -- as particle size -- 0.1-0.5 micrometers -- mean particle diameter within the limits -- suitable -- of course -- a resin solution -- fitness -- what performed surface treatment may be used so that it may have dispersion power.

[0062] Although a polymerization is performed in the conventional polymerization method after cheating out of a coloring agent distribution (differential powder) minutely in a monomer, like a monomer, it can come that stability carries out differential powder of the coloring agent to the thing of hypoviscosity, and it is difficult again.

[0063] It is also difficult to prevent condensation of the coloring agent in the middle of performing the polymerization in addition to it. So, as long as it is based on a polymerization method, it can be said to be very difficult to make distribution of the coloring agent in a particle into homogeneity even if it uses a distributed stabilizer.

[0064] It is possible for the differential powder of the coloring agent to be easily carried out into resin on the other hand using the conventional distributed technique according to this invention also in an amount which it says with carbon is 30 % of the weight, for example, even if it makes it the content of a coloring agent from the first.

[0065] Furthermore, since the second process can attain particle-izing and capsulation in an instant, with this condition maintained, distribution of the coloring agent in a particle has the description of being accomplished by homogeneity.

[0066] That is, the second process is the phase of performing phase inversion emulsification into a water medium, after neutralizing primarily the anion mold self-moisture acidic resin which carries out mixed distribution of the coloring agent by the base.

[0067] After being neutralized by the base, by adding a water medium and going, conversion of the resin phase from W/O to O/W is performed in an instant, and the particle which contained the coloring agent in the water medium generates the self-water-dispersion resin which carried out distributed mixing of the coloring agent.

[0068] In this case, resin is adsorbed and a coloring agent is incorporated inside a particle. It is used in order to carry out localization of the hydrophilic part to a particle front face and to maintain a stable configuration in a water medium including the acid radical neutralized by the base.

[0069] by the way, the conventional polymerization method -- if -- with formation-ization of a rough capsule unit particle, i.e., the particle of a unit which can serve as a capsule although it still becomes a capsule and is not, (the base for wallplates -- a raw material being contained) first. Then, it consists of two processes with formation-izing of a capsule wall, and, moreover, performed as a separate process of the form where each process became independent.

[0070] On the other hand, in this invention, both the above-mentioned processes are distinguished, without being distinguished, it is using phase inversion emulsification of self-moisture acidic resin, and the description is in the point of completely going on being simultaneous and completely in an instant.

[0071] Therefore, the condition of having carried out differential powder to resin will be maintained, the distributed condition of a coloring agent cannot be overemphasized, and this coloring agent will be distributed to homogeneity in a particle. And since a desiccation particle front face is completely covered by resin, it serves as a place where the variation in the electrification property resulting from a coloring agent is also solved.

[0072] Subsequently, in addition to formation of a capsule, control of the particle size used as another important factor is included in the second process in this invention. It is controlled in the amount of the base which neutralizes fundamentally the acid radical contained in anion mold self-moisture acidic resin.

[0073] the amount of neutralization (amount of the base which neutralization takes) according [ on the approach of this invention, and ] to a base suitably -- 10-100 mol% of an acid radical -- the thing of the particle size from submicron (less than 1 micron) one to 30 micrometers can be obtained to arbitration by making it change by within the limits.

[0074] The ease of control of this particle size also becomes one description of this invention. As a toner for high resolving, \*\* and correspondence are possible also for the needs as which 5-micrometer particle level is being required.

[0075] And the capsule mold toner particle which succeeds in normal distribution is obtained substantially, without particle-izing and capsulation in a water medium providing any special means, if various kinds of solvents and solutes have applied the share of extent mixed by homogeneity, since the self-dispersion power of resin called phase inversion emulsification is used.

[0076] Here, if the share to phase inversion is too weak, the inclination for particle size distribution to spread will surely be seen. Moreover, if a share is too too strong, the generated toner particle will be destroyed, and an aggregate and a very detailed particle will arise, as a result distribution will spread.

[0077] In this invention, if it carries out from the field that a capsule wall is formed in an instant, it can be considered that they are near and the thing of the form where near, therefore this invention united these both-hands methods with physicochemical technique when carrying out from the field of phase conversion on the other hand at more mechanical technique.

[0078] From the place which is what makes normal distribution and is obtained, though the capsule mold toner of this invention classifies particle size distribution further in order to arrange, it should just carry out a classification only within a part.

[0079] It is going by the form returned to the first process in addition, and the toner classified in this way is remelted to a solvent, and is easy to reuse. The third process obtains a powder-like dry capsule particle except for an organic solvent or a water medium.

[0080] the capsule mold toner particle obtained at the second process -- water -- and -- an organic solvent -- since it is distributing in a medium, vacuum distillation removes an organic solvent first. This organic solvent has the desirable thing of a low-boiling point from the place distilled off easily.

[0081] Subsequently, by suction filtration, after obtaining the wet cake of a toner particle, it can dry with a jet mill etc., or a powder-like capsule mold toner particle can be obtained by the approach of well-known common use of a spray dryer etc.

[0082] The inclination which the capsule mold toner particle obtained by this invention is a desiccation process, and condenses and welds it by the interaction between particles depending on the case from the place where the acid radical with which the acid radical was neutralized by the base above all has covered the front face is seen.

[0083] After such a problem completes capsulation at the second process, you make it reverse-neutralize and it is \*\*\*\*(ed) by an inorganic acid or the organic acid by returning to an acid. Namely, by back-ization to the acid by such reverse neutralization, the stability in the inside of a water medium is made to lose, and it closes, and

make separation with a water medium easy, moreover the interaction between particles is made to lose by it, and it closes, and protects the welding of a under [ desiccation ].

[0084] In this case, as for the particle dried by the technique of well-known common use of filtration or the spray-drying method, condensation or welding are not accepted at all. Moreover, a place to a problem excellent in the stability with the passage of time under high-humidity/temperature cannot be found about an electrification property, either.

[0085] To the offset phenomenon of a toner, this is improvable if needed by blending various kinds of waxes like polyethylene wax, a polypropylene wax, carnauba wax, or a silicon system compound.

[0086] In this invention, it is the first process of carrying out mixed distribution of resin and the coloring agent, and it is possible by adding such waxes and carrying out mixed distribution into resin like a coloring agent for you to make it homogeneity distributed and mixed in a particle.

[0087] Within the limits which becomes 0.1 to 5% of the weight to the resin solid content containing a coloring agent as loadings of such an additive is suitable. In this invention, it is also possible to blend a charge control agent.

[0088] As the addition approach, like the above-mentioned waxes, in the first process, it can be added in the phase which carries out mixed distribution of a coloring agent and the resin, and can be incorporated into a particle. That is, this charge control agent is incorporated to the strong particle front face of a hydrophilic property, and gives a desired electric charge property (electrification property).

[0089] Within the limits which becomes 0.1 to 5% of the weight to the resin solid content containing a coloring agent as loadings of a charge control agent is suitable.

[0090]

[Example] Next, the example of reference and an example explain this invention much more concretely. Unless the section and % have a notice especially in below, they shall be weight criteria altogether.

[0091] Example of reference 1 (example of preparation of anion mold self-water-dispersion resin)

The 200 sections of a methyl ethyl ketone were put into the reactor, were heated, and it was made 80 degrees C. Subsequently, the mixture of a rate as shown below was dropped for about 2 hours. In the meantime, the reaction was performed in the nitrogen air current.

[0092]

Methacrylic acid Section [ 22.5 / ] Styrene "Par Butyl O" [Fault 3 Section Oxidation \*\*\*\*\* by Nippon Oil & Fats Co., Ltd.] <BR> 227 Section 2-ethylhexyl Acrylate 33 Section Methyl Methacrylate 37.5 Sections Methyl ethyl ketone 12 The 0.25 sections of "par butyl O" are added over the after 2 hours, subsequently to 80 degrees C, it held for 24 hours and the reaction was made to add the 0.25 sections of "par butyl O" to reaction mixture, and to continue further 1 hour after the dropping termination of mixture which carried out the section above.

[0093] The solution of the copolymer with which the heating residue becomes 53.8% was obtained after reaction termination.

Example of reference 2 (same as the above)

It reacted by dropping the mixture of a rate as shown below like the example 1 of reference.

[0094]

Methacrylic acid 45 Section "Par Butyl O" [Fault 3 Section Oxidation \*\*\*\*\* by Nippon Oil & Fats Co., Ltd.]

<BR> Styrene 207 Section 2-ethylhexyl Acrylate 33 Section Methyl Methacrylate 15 Section Methyl ethyl ketone 12 The solution of the copolymer with which the heating residue becomes 54% was obtained after section reaction termination.

[0095] Example of reference 3 (same as the above)

a reaction container -- -- putting in and stirring the 30 sections of BUREMMA ME-4000" [the monomer by Nippon Oil & Fats Co., Ltd.], and the 150 sections of n-butanol, it heated to 40 degrees C and the individual was made to dissolve completely

[0096] Polymerization nature monomers mixture was adjusted as follows, and was changed.

Methacrylic acid 18 Section "Par Butyl O" [Fault 3 Section Oxidation \*\*\*\*\* by Nippon Oil & Fats Co., Ltd.]

<BR> Styrene 90 Section 2-ethylhexyl Acrylate 33 Section Methyl Methacrylate 129 Section n-butanol 12 It is "BUREMMA in a reaction container in 15% of the mixed solution of \*\*\*\*. After in addition to a ME-4000"-n-butanol solution mixing to homogeneity and carrying out a temperature up to 90 degrees C, the remaining mixture was dropped for about 2 hours.

[0097] After that, kept at 90 degrees C, the reaction between 5 hours was made to continue, and anion mold self-moisture acidic resin was obtained.

Example The example of one is an example of preparation of an amine salt type carbon toner.

[0098] Having added the 12.8 sections of dimethylamino ethanol and stirring in 2,500RPM using TK homomixer, water was dropped at the thing which made the 200 sections of anion mold self-water-dispersion resin and the 11.9 sections of "MA-100 [the carbon black made from Mitsubishi Kasei Industry]" which were obtained in the example 1 of reference mix for 1 hour by "Eiger motor mill M-250 VSE-EXJ [the Eiger product]", and phase inversion emulsification was performed to it.

[0099] Vacuum distillation removed the organic solvent and the moisture acid liquid of an amine salt type carbon toner was obtained. Subsequently, this was made to dry with a spray dryer and the toner powder made into the purpose was obtained.

[0100] the description of the carbon toner obtained by this example — a value is shown in the 1st table. Moreover, the place which copied the chart for a test using this toner, and the reproducible image were obtained, and it was checked that it is what can be equal to actual use.

[0101] Example The example of two is an example of preparation of a carboxylic-acid mold carbon toner. The 0.01-N hydrochloric-acid water solution was slowly added until pH of the moisture acid liquid of the amine salt type carbon toner obtained in the example 1 was set to 6.

[0102] You made it dry by the spray dryer method, and the powder of the carboxylic-acid mold carbon toner made into the purpose was obtained. the description of the carbon toner obtained by this example — a value is shown in the 1st table.

[0103] Moreover, the place which copied the chart for a test using this toner, and the reproducible image were obtained, and it was checked that it is what can be equal to actual use.

Example The example of three is also an example of preparation of a carboxylic-acid mold carbon toner.

[0104] Having added the five sections of dimethylamino ethanol and stirring in 350RPM using a three one motor, water was dropped at the thing which made the 200 sections of the anion mold self-water-dispersion resin obtained in the example 2 of reference, the 65 sections of a methyl ethyl ketone, and the 5.6 sections of "MA-100" mix for 1 hour by "Eiger M-250 VSE-EXJ", and phase inversion emulsification was performed to it.

[0105] The 0.01-N hydrochloric-acid water solution was slowly added until vacuum distillation removed the organic solvent and acidity or alkalinity was set to pH6. Subsequently, the toner powder which is made to dry table-top-type spray dryer SD-1 mold by spray dryer [Tokyo Rika Co., Ltd. by use], and targets this was obtained.

[0106] the description of the carbon toner obtained by this example — a value is shown in the 1st table. Moreover, the place which copied the chart for a test using this toner, and the reproducible image were obtained, and it was checked that it is what can be equal to actual use.

[0107] Example The example of four is also an example of preparation of a carboxylic-acid mold carbon toner. Having added the 3.4 sections of dimethylamino ethanol and stirring in 250RPM using TK homomixer, water was dropped at the thing which made the 200 sections of the anion mold self-water-dispersion resin obtained in the example 3 of reference, the 65 sections of a methyl ethyl ketone, and the 11.9 sections of "MA-100" mix for 1 hour by "Eiger M-250 VSE-EXJ", and phase inversion emulsification was performed to it.

[0108] The 0.01-N hydrochloric-acid water solution was slowly added until vacuum distillation removed the organic solvent and acidity or alkalinity was set to pH6. Subsequently, this was made to dry with a spray dryer and the toner powder made into the purpose was obtained.

[0109] The average grain of a toner measured by the coal tar Marti sizer is 10.8 micrometers, and 5-micrometer or more toner 20 micrometers or less was obtained with the yield which becomes 85.8%.

[0110] Example The example of five is an example of preparation of a magnetic toner. the 200 sections of the anion mold self-water-dispersion resin obtained in the example 1 of reference, and the 65 sections of a methyl ethyl ketone — and — " — the thing which made the 100 sections of MABIKO black BL-500" [the tri-iron tetraoxide powder by Titan Kogyo K.K.] mix for 2 hours by "Eiger M-250 VSE-EXJ" Having added the 13.5 sections of dimethylamino ethanol and stirring in 350RPM using a three one motor, water was dropped and phase inversion emulsification was performed.

[0111] The 0.01-N hydrochloric-acid water solution was slowly added until vacuum distillation removed the organic solvent and acidity or alkalinity was set to pH6. Subsequently, this was made to dry with a spray dryer and the toner powder made into the purpose was obtained.

[0112] The average grain of a toner measured by the coal tar Marti sizer is 10 micrometers, and 5-micrometer or more toner 20 micrometers or less was obtained with the yield which becomes 80%.

[0113]

[Table 1]

第 1 表			実施例 1	実施例 2	実施例 3
着 色 剤 含 有 量 (%)			1 0	1 0	5
粒 1) 度 分 布	平均粒径 (μm)		8. 4	8. 4	9. 3
	有効粒径内粒子量 (%)		8 7. 8	8 4. 0	8 6. 5
	分級後の平均粒子径		9. 4	9. 7	9. 3
帯 2) 3) 電 電 荷 量  (μc /g)	10℃, 30%	A	-18. 3	-19. 1	-34. 5
		B	-18. 5	-20. 0	-33. 5
		C	-18. 2	-18. 2	-31. 6
	25℃, 55%	A	-17. 4	-19. 6	-35. 2
		B	-24. 5	-23. 8	-41. 5
		C	-25. 5	-25. 6	-40. 5
	35℃, 85%	A	-26. 1	-23. 3	-39. 5
		B	-26. 2	-23. 5	-43. 3
		C	-31. 3	-27. 3	-43. 5

[0114] 1st table \*\*\*\*\* 1 It is the value measured by the coal tar Marti sizer.

\*\* 2 As a measuring method, the developer set to 1g of a toner from "TSV-200DC #906074 [the Powdertech carrier]" is made into a sample, and it is the low temperature which becomes \*\* 10 degrees C about this sample, respectively, And it is the conditions that it is damp 30%, the conditions of \*\* ordinary temperature (25 degrees C) and normal relative humidity (55%), and \*\* 35-degree-C the becoming elevated temperature, and was left for 16 hours under each environment of the conditions that it is highly humid 85%.

[0115] Subsequently, 1 time amount carried out the between charge up of this by 238RPM with the ball mill, and the amount of electrifications was measured. This result was made into "measured value A."

[0116] The amount of electrifications was measured also with the case where a sample same as the above is left by each environment further same as the above for 24 hours. This result was made into "measured value B."

[0117] After measurement of such measured value B, again, the charge up was performed for 10 minutes and, subsequently the amount of electrifications was measured. This result was made into "measured value C."

[0118] All of the unit of an electrification loading dose are a microcoulomb ( $\mu\text{c}$ )/g.

\*\* 3 On the occasion of measurement, the classification removed 5-micrometer or more particle 20 micrometers or less of each toner.

[0119]

[Effect of the Invention] According to this invention, the capsule mold toner particle which does not contain a distributed stabilizer and which the coloring agent distributed in the particle to homogeneity can be obtained in the easy process which is not in the former. Particle size is easily controlled in the amount of the base which neutralizes an acid radical substantially. Moreover, since particle size distribution use the physicochemical phenomenon of phase inversion emulsification of resin, what makes normal distribution is obtained.

[0120] Since various kinds of anion mold self-water-dispersion resin can be used for the resin which forms a

particle, desired properties, such as an electrification property, a fluidity, and fixable, are easy to be acquired. A coloring agent can also use the thing of arbitration. The capsule mold toner particle obtained by this invention does not have the effect on [ from the place where the particle front face is completely covered by resin ] the surface charge by the coloring agent, and it succeeds also in the correspondence to a color toner easily.

[Translation done.]

(19)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平5-66600

(43)公開日 平成5年(1993)3月19日

(51)Int.Cl. <sup>4</sup>	識別記号	庁内整理番号	FI	技術表示箇所
G 0 3 G 9/08 9/087	3 1 1	7144-2H  7144-2H 7144-2H	G 0 3 G 9/ 08	3 2 1 3 8 1

審査請求 未請求 請求項の数10(全 11 頁)

(21)出願番号 特願平3-224227

(22)出願日 平成3年(1991)9月4日

(71)出願人 000002886

大日本インキ化学工業株式会社  
東京都板橋区坂下3丁目35番58号

(72)発明者 田代 南征

千葉県袖ヶ浦市長浦駅前7-4-6

(72)発明者 高柳 均

千葉県佐倉市六崎田1550-2

(72)発明者 新堂 宏子

千葉県佐倉市六崎54 サザンホワイト102号

(74)代理人 弁理士 高橋 勝利

(54)【発明の名称】 カプセル型トナーおよびその製造方法

(57)【要約】 (修正有)

【構成】着色剤がアニオン型自己水分散性樹脂に内包されたカプセル型トナーであって、一例として、アニオン型自己水分散性樹脂の100部と、着色剤の2~150部とからなる両成分を、混合分散する第一工程と、これを転相乳化することで、水媒体中にカプセル化された粒子を生成させる第二工程と、生成したカプセル粒子を、水媒体中から分離し乾燥する第三工程とから成る、カプセル型トナーの製造方法。

【効果】分散安定剤を含まない、着色剤が均一に粒子内に分散したカプセル型トナー粒子を、簡単なプロセスで得ることができる。粒径は酸基を中和する塩基の量で容易にコントロールされ、粒度分布も正規分布をなす。又、各種のアニオン型自己水分散性樹脂を用いることにより、所望の特性(帯電性、流動性、定着性など)が得られる。